PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C09K 21/14, 21/02, 21/06

A1

(11) International Publication Number: WO 96/20987

(43) International Publication Date: 11 July 1996 (11.07.96)

(21) International Application Number: PCT/US95/16633

(22) International Filing Date: 19 December 1995 (19.12.95)

(30) Priority Data:
08/366,959 30 December 1994 (30.12.94) US
08/567,956 6 December 1995 (06.12.95) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventor: WELNA, Walton, W.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: ALLEN, Gregory, D. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

= WO 9578671

(54) Title: INTUMESCENT PUTTY

(57) Abstract

This invention relates to non-aqueous, indefinitely conformable, halogen free, intumescent putty useful in an opening as a firestop material to deter the spread of fire, smoke, and vapors during a fire.

INTUMESCENT PUTTY

Field of the Invention

This invention relates to intumescent putty for use in an opening as a firestop material to deter the spread of flame, smoke, and vapors during a fire.

Description of Related Art

Firestop products are used to reduce or eliminate the chimney effect at through-penetrations. Characteristics of firestop materials suitable for typical commercial uses include the ability to expand and to char. Further, the charred material preferably has sufficient strength to withstand a hose stream test.

An industry recognized fire endurance test used to evaluate firestop materials is the American Society of Testing Materials' test identified as "ASTM E-814-83." This test includes subjecting the charred material to a stream of water from a fire hose.

Summary of the Invention

The present invention provides a non-aqueous, indefinitely conformable, halogen-free, intumescent putty comprising a blend of intumescent material, rubber, and unvulcanized rubber, the rubber and unvulcanized rubber together provide the putty with a softness value of at least 4 mm (preferably, at least 4.5 mm; more preferably at least 5 mm; and even more preferably, at least 6 mm). Further, the putty is

In this application:

"putty" refers to a cohesive, moldable material that does not substantially flow at ambient temperatures (typically temperatures in the range from about 0°C to about 50°C);

"indefinitely conformable" means the putty remains soft and handleable for at least one month, (preferably, one year; more preferably, at least five years; even more preferably, at least ten years; and most preferably, at least twenty years) under ambient temperatures (typically temperatures in the range from about 0°C to about 50°C);

"halogen-free" means essentially free of halogens (i.e., contains less than 0.25 percent (preferably, less than 0.1 percent; more preferably, less than 0.01 percent) by weight halogen calculated on an elemental basis as Cl, F, etc., based on the total weight of the putty;

"non-aqueous" means essentially free of (i.e., contains less than 0.25 percent by weight) water, other than bound water, wherein bound water is water that does not come off until the material is heated to at least 100°C (preferably, at least 150°C, more preferably, at least 250°C);

"intumescent" refers to a material which expands upon heating above about 100°C, although the temperature at which a particular intumescent material intumesces is dependent on the composition of that material;

"intumescent putty" refers to a putty that intumeces to at least two times (preferably at least three times) its (original) unexpanded volume (i.e., its volume prior to intumescing);

the intumescence, softness, and flame retardance properties of the putty; and

"char strength" is a measure of the strength of the expanded carbonaceous residue ("char") formed from the putty after exposure to temperatures above about 350°C for about 15 minutes.

Intumescent putties according to the present invention typically are reuseable, exhibit good adhesion properties, and can be used to restore acceptable fire ratings of floors and walls after penetrations (or openings) are made in them. Such penetrations are made, for example, to accommodate the passage of cables, conduits, metal and plastic pipe, and telephone installations. If the penetrations or openings around the installations that pass through the penetrations are not adequately sealed, flame, smoke, and/or water may pass there through and extend the destruction of a fire and/or water damage.

Description of Preferred Embodiments

The intumescent putty according to the present invention remains in a soft, pliable, and unexpanded condition until it is exposed to heat at temperatures in excess of about 100°C (212°F). When heated above about 350°C (662°F), the putty readily intumesces typically to about three times its original volume, and begins to form char that further enhances the putty's flame retardant characteristics. The putty seals voids in through-penetrations caused by burning and/or melting materials, effectively preventing the passage of flame, smoke, vapors, and water from one location (e.g., a room or floor) to another.

A preferred rubber is a styrene butadiene rubber, characterized by the manufacturer as having a high degree of crosslinking (commercially available under th trade designation "POLYSAR S1018" from Polysar Rubber Div. of Miles, Inc.). A styrene butadiene rubber, characterized by the manufacturer as having a low Mooney viscosity (commercially available from Ameripol Synpol Co., a Division of Uniroyal Goodrich Tire Co. of Akron, OH) is the preferred unvulcanized rubber.

In a preferred embodiment, two types of rubbers are used together with an unvulcanized rubber. The first rubber is preferably a styrene butadiene rubber, characterized by the manufacturer as having a high degree of crosslinking ("POLYSAR S1018"). The amount of this rubber preferably ranges from about 10 to about 40 percent by weight of the total rubber and unvulcanized rubber content of the putty. The second rubber is preferably a butyl rubber characterized by the manufacturer as "moderately" crosslinked" (commercially available under the trade designation "POLYSAR BUTYL XL 68102" from Polysar Rubber Div. of Miles, Inc. of Akron, OH). This second rubber is believed to provide a desirable level of stretch. Preferably, the amount of this rubber ranges from about 1 percent by weight to about 5 percent (more preferably, about 1 to about 2 percent) by weight of the total rubber and unvulcanized rubber content of the putty. If the amount of moderately crosslinked rubber is greater than about 5 percent by weight, the material tends to be undesirably tacky, and may be difficult to install in some applications. At levels of less than 1 percent by weight, typically no benefit in stretch is observed from its addition to the formulation.

forms in a fire such that heated putty does not pass the Fire Hose Stream Test described below.

Typically, the amount of intumescent hydrated alkali metal silicate used ranges from about 50 to about 200 percent (preferably about 100 to about 140 percent) by weight of the total rubber and unvulcanized rubber content of the putty. In another aspect, the hydrated alkali metal silicate preferable is present in the range from about 5 to about 45 percent by weight, based on the total weight of the putty.

The hydrated alkali metal silicate particles typically range in size from about 75 micrometers to about 500 micrometers.

A silicate intumescent material is preferably used together with a silicate fluxing agent such as boric oxide. Such fluxing agents are used to stabilize the char formed when the putty is subjected to heat. A preferred silicate fluxing agent is anhydrous boric oxide (B_2O_3), commercially available from U.S. Borax of Valencia, CA. Boric oxide can function as both a flame retardant and a silicate fluxing agent.

If the intumescent material is intercalated graphite, the putty preferably comprises in the range from about 5 to about 30 percent by weight intumescent material, based on the total weight of the putty.

It is within the scope of the present invention to use combinations of intumescent material (e.g., to use both hydrated alkali metal silicate and intercalated graphite).

Preferably, a sufficient amount of plasticizer is included in the putty to obtained the desired level of softness and moldability. Plasticizers are compounds that increase the flexibility of a material and facilitate processing. Suitable plasticizers include

from Allright & Wilson Ltd. of Richmond, VA), dimelamine phosphate (commercially available, for example, under the trade designation "AMGUARD ND" from Allright & Wilson Ltd.), melamine phosphate (commercially available, for example, under the trade designation "AMGUARD NH" from Allright & Wilson Ltd.), ammonium polyphosphate (commercially available, for example, under the trade designations "PHOS CHEK P30" and "PHOS CHEK P40" from Monsanto); and a blend of bis melaminium pentate and polyhedric oxide (commercially available, for example, under the trade designation "CHAR GUARD 329" from Great Lakes Chemical Corp. of West Lafayette, IN).

Useful char forming resins include epoxy resins, phenolic resins, polycarboimide resins, urea-formaldehyde resins, and melamine-formaldehyde resins. The general term "phenolic" refers to phenol-formaldehyde resins as well as resins comprising other phenol-derived compounds and formaldehydes. A preferred char forming resin is an epoxy resin commercially available under the trade designation "SCOTCHCAST SR 265" from the 3M Company of St. Paul, MN.

Fillers can used to adjust the hardness of the putty (i.e., fillers typically make the putty stiffer or harder), act as reinforcement, or reduce cost. Fillers include fumed silica, clay, fly ash, colorants, perlite, vermiculite, inorganic fibers (e.g., glass fibers and mineral fibers), and organic fibers. Melamine, which as discussed above is an organic intumescent material, is also useful as a filler to adjust the tack of the putty. A preferred filler is milled glass fiber (commercially available as "731ED FIBERGLAS" from Owens-Corning Fiberglas Corp. of

melamine, antioxidants, and antiozonants are then added while the mixing operation continues. Plasticizer is typically added and then mixed in for a few minutes. The last ingredient added is usually the intumescent material. The putty is typically mixed until homogeneous and smooth (i.e., not lumpy). After mixing, the putty is ready to use.

For many firestop applications, the putty is typically extruded into sheets or pads (usually about 0.635 cm (0.25 inch thick). The sheets or pads are cut to provide the desired size or shape for a particular application. For some applications, the putty is formed into sticks or rope.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

Softness Value Measurement

The softness of the putty is determined using a penetrometer (available as Model 73510 from Precision Instruments of Chicago, IL). Measurement of the softness of the putty involves dropping a weighted cone-shaped object into the putty, and then measuring the distance the object penetrates the putty. The test procedure is described in ASTM D-1403-91, which is entitled "Standard Test Methods for Cone Penetration of Lubricating Grease Using One-Quarter and One-Half Scale Cone Equipment," wherein the penetration measurements were made using a stainless steel, quarter scale cone as specified in the ASTM test method.

Flame Through Test

The Flame Through Test follows the procedure set forth in ASTM (American Society for Testing Materials) Test "E 814-83," entitled "Standard Test Method for Fire Tests of Through-Penetration Fire Stops", incorporated herein by reference. This test is used to evaluate the use of putty in a through-penetration fire application.

For this test, a poured concrete slab, 11.4 cm (4.5 in) thick and approximately 30.5 cm (3 ft) square, was prepared. Four 10.2 cm (4 in) diameter circular openings were made in the slab. The openings were evenly spaced. A 2.5 cm (1 in)) thick mineral fiber insulation material (commercially available under the trade designation "USG #4 FIRE SAFING" from US Gypsum of Chicago, IL) was firmly packed into each opening in the slab. The mineral fiber was recessed about 2.5 cm from the top surface of the concrete. The putty was packed into the opening flush with the top surface of the concrete. The thickness of the putty was about 2.5 cm. The concrete slab was placed on the top of a gas-fired furnace (commercially available from Armil C.F.S. of South Holland, IL). The mineral fibers faced the heat source (flame) of the furnace.

The time and temperature parameters outlined in Figure 1 of ASTM E 814-83 were followed for the test. The test was run for 3 hours, unless flame through occurred. Flame through is indicated by flames coming through the opening to the "cold" side of the concrete slab. If there is flame through in less than 3 hours, then the material tested is deemed to have failed the test. If the opening remained sealed for the 3 hours, then the fire stop is given a passing designation (referred in ASTM E 814-83 as having an "F" rating).

The ingredients used for the examples are listed in Table 1, below.

Table 1

Ingredient	Trade Designation	Source of Ingredient
Unvulcanized styrene butadiene rubber	"AMERIPOL SYNPOL 8107"	Ameripol Synpol Co. Division of Uniroyal Goodrich Tire Co., Akron, OH
Styrene butadiene rubber	"POLYSAR S 1018"	Polysar Rubber Division of Miles, Pittsburgh, PA
Moderately crosslinked butyl rubber	"POLYSAR BUTYL XL 68102"	Polysar Rubber Division of Miles, Pittsburgh, PA
Mixture of diaryl p-phenylene diamine	"WINGSTAY 100"	Goodyear Chemicals Division of Goodyear Tire and Rubber Co., Akron, OH
Thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate	"IRGANOX 1035"	Additives Division of Ciba-Geigy Corp., Hawthorne, NY
Fumed silica	"CAB-O-SIL M-5"	Cabot Corp., Tuscola, IL
Epoxy resin powder	"SCOTCHCAST SR-265"	The 3M Company, St. Paul, MN
Powdered iron oxide (Fe_2O_3)	"IRON OXIDE BF-95"	Bailey Engineers, Inc., Fairfield, AL
Boron trioxide powder	"ANHYDROUS BORIC ACID"	U.S. Borax, Valencia, CA
Melamine powder (-60 mesh)	"AERO MELAMINE"	Cytec Industries, West Peterson, NJ
Milled glass filaments	"731ED FIBERGLASS 1/8""	Owens-Corning, Fiberglas Corp., Toledo, OH

Examples 1 and 2

The ingredients for Examples 1 and 2 are listed in Table 2, below.

Table 2

Ingredient	Amount of Ingredients, PHR* Example 1	Example 2
Unvulcanized styrene butadiene rubber ("AMERIPOL SYNPOL 8107")	76.50	76.50
Styrene butadiene rubber ("POLYSAR S 1018")	20.00	20.00
Moderately crosslinked butyl rubber ("POLYSAR XL 68102")	3.50	3.50
Mixture of diaryl p-phenylene diamine ("WINGSTAY 100")	2.00	2.00
Thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate ("IRGANOX 1035")	2.00	2.00
Fumed silica ("CAB-O-SIL M 5")	13.00	13.00
Epoxy resin powder ("SCOTCHCAST SR 265")	15.00	15.00
Powdered iron oxide (Fe_2O_3) ("IRON OXIDE BF 95")	5.00	5.00
Melamine powder ("AERO MELAMINE")	50.00	75.00
Boron Oxide (Anhydrous)	40.00	40.00
Milled glass filaments ("731ED FIBERGLASS")	30.00	30.00
Isobutylene butene copolymer liquid ("INDOPOL H 100")	40.00	50.00
Petrolatum ("6916 WAX")	60.00	60.00
Granulated hydrated sodium silicate ("EXPANTROL 4BW")	120.00	
Intercalated graphite flake ("GRAPHITE TG 326")		70.00

* Parts per hundred based on the total rubber and unvulcanized rubber content of the putty.

The ingredients for each example were compounded using an internal mixer (Prep Mixer, Part # 02-22-000, 350/420 cm^3 capacity; available from C. W. Brabender Instruments, Inc. of South Hackensack, NJ) equipped with sigma mixing blades. The mixer was powered by a

it in molten paraffin wax, submerging and weighing the (coated) disc in deionized water, and then calculating the volume using the following equation:

$$\text{volume} = \frac{\text{dry weight - submerged weight}}{\text{density of water}} \quad \text{(Equation 1)}$$

The disc was then placed in a muffle furnace at about 350°C for about 15 minutes to intumesce and char. The resulting charred, expanded disc was then weighed, coated with wax, and then submerged and weighed in deionized water. The volume of the charred, expanded disc was calculated using Equation 1 (above).

The expansion ratio was calculated using the following equation:

$$\text{volume} = \frac{\text{volume of charred, expanded disc}}{\text{volume of initial (uncharred) disc}} \quad \text{(Equation 2)}$$

The expansion ratios of Examples 1 and 2, based on an average of two determinations, were 2.84 and 5.22, respectively. The flow characteristics of the Example 1 and 2 putties were both excellent.

Examples 1 and 2 passed both the "Flame Through Test" and the "Fire Hose Stream Test."

Examples 3-10

The ingredients for Examples 3-10 are listed in Table 3, below.

Table 3, Continued

	Amount of ingredients, PHR							
Ingredient	**Ex. 3**	**Ex. 4**	**Ex. 5**	**Ex. 6**	**Ex. 7**	**Ex. 8**	**Ex. 9**	**Ex. 10**
Melamine powder ("AERO MELAMINE")	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Boron Oxide (Anhydrous)	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Milled glass filaments ("731ED FIBERGLASS")	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Isobutylene butene copolymer liquid ("INDOPOL H 100")	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Petrolatum ("PAXWAX 5324")	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
Granulated hydrated sodium silicate ("EXPANTROL 4BW")	120.00	120.00	120.00	120.00	120.00	120.00	120.00	120.00

Examples 11-14

The ingredients for Examples 11-14 are listed in Table 4, below.

Table 4

	Amount of ingredients, PHR			
Ingredient	**Ex. 11**	**Ex. 12**	**Ex. 13**	**Ex. 14**
Unvulcanized styrene butadiene ("AMERIPOL SYNPOL 8107")	76.50	76.50	76.50	76.50
Styrene butadiene rubber ("POLYSAR S 1018")	20.00	20.00	20.00	20.00
Moderately crosslinked butyl rubber ("POLYSAR XL 68102")	3.50	3.50	3.50	3.50
Mixture of diaryl p-phenylene diamine ("WINGSTAY 100")	2.00	2.00	2.00	2.00
Thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate ("IRGANOX 1035")	2.00	2.00	2.00	2.00
Fumed silica ("CAB-O-SIL M 5")	13.00	13.00	13.00	13.00
Epoxy resin powder ("SCOTCHCAST SR 265")	15.00	15.00	15.00	15.00
Powdered iron oxide (Fe_2O_3) ("IRON OXIDE BF 95")	5.00	5.00	5.00	5.00
Melamine powder ("AERO MELAMINE")	50.00	50.00	50.00	50.00
Boron Oxide (anhydrous)	40.00			
Hydrated Zinc Borate ("FIREBRAKE ZB FINE")		40.00		83.25
Milled glass filaments ("731ED FIBERGLASS")	30.00	30.00	30.00	30.00
Isobutylene butene copolymer liquid ("INDOPOL H 100")	40.00	40.00	40.00	40.00
Petrolatum ("PAXWAX 5324")	60.00	60.00	60.00	60.00
Granulated hydrated sodium silicate ("EXPANTROL 4BW")	120.00	120.00	120.00	120.00

Examples 11-14 were prepared by blending the styrene butadiene rubbers ("POLYSAR S 1018" and "POLYSAR XL 68102"), and about 4.35% of the unvulcanized styrene butadiene rubber ("AMERIPOL SYNPOL 8107") on a 40.6 cm (16 inch) rubber mill, and then mixing for about 30 minutes at about 20 rpm. About 3.75% of the plasticizer ("INDOPOL H-100") was then added to the rubber/unvulcanized rubber mixture while milling continued.

samples, however, passed the "Flame Through Test." For the "Hose Stream Test," four of the Example 11 samples pass d, one of the Example 12 samples passed, none of the Example 13 samples passed, and three of the Example 14 samples passed.

Examples 15-19

The ingredients for Examples 15-19 are listed in Table 5, below.

TABLE 5

	Amount of ingredients, PHR				
Ingredient	**Ex. 15**	**Ex. 16**	**Ex. 17**	**Ex. 18**	**Ex. 19**
Unvulcanized styrene butadiene rubber ("AMERIPOL SYNPOL 8107")	76.50	76.50	76.50	76.50	76.50
Styrene butadiene rubber ("POLYSAR S 1018")	20.00	20.00	20.00	20.00	20.00
Moderately crosslinked butyl rubber ("POLYSAR XL 68102")	3.50	3.50	3.50	3.50	3.50
Mixture of diaryl p-phenylene diamine ("WINGSTAY 100")	2.00	2.00	2.00	2.00	2.00
Thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate ("IRGANOX 1035")	2.00	2.00	2.00	2.00	2.00
Fumed silica ("CAB-O-SIL M 5")	13.00	13.00	13.00	13.00	13.00
Epoxy resin powder ("SCOTCHCAST SR 265")	15.00	15.00	15.00	15.00	15.00
Powdered iron oxide (Fe_2O_3) ("IRON OXIDE BF 95")	5.00	5.00	5.00	5.00	5.00

all had a good level of tackiness and left no visible residue on the skin.

Example 20

The ingredients for Example 20 are listed in Table 6, below.

Table 6

	Amount of ingredients, PHR
Ingredient	**Example 20**
Non-crosslinked styrene butadiene rubber ("AMERIPOL SYNPOL 8107")	80.00
Cross-linked styrene butadiene rubber ("POLYSAR S 1018")	20.00
Fumed silica ("CAB-O-SIL M-5")	13.00
Epoxy resin powder ("SCOTCHCAST SR 265")	15.00
Powdered iron oxide (Fe_2O_3) ("IRON OXIDE BF 95")	5.00
Hydrated zinc borate ("FIREBRAKE ZB FINE")	50.00
Chopped fiberglass fibers ("799AB")	20.00
Isobutylene butene copolymer liquid ("INDOPOL H 100")	71.00
Blend of bis melaminium pentate and polyhedric oxide ("CHARGUARD 329")	15.00
Petrolatum ("PETROLATUM RPB")	50.00
Granulated hydrated sodium silicate ("EXPANTROL 2")	100.00

Example 20 was prepared as described for Examples 1 and 2. The batch size was about 439 grams.

The expansion ratio of Example 20 was determined (as described in Examples 1 and 2) to be 7.05. The softness value was determined as described above under the heading "Softness Value Measurement" to be 5.6 mm. The flow characteristic of the putty was good.

Example 20 passed both the "Flame Through Test" and the "Fire Hose Stream Test."

and milled glass fibers were added while mixing continued. The ingredients were mixed for about 3 minutes, after which the mixing spe d was increased to about 60 rpm. The plasticizer ("INDOPOL H-100") was then added, and mixing continued for about 13 minutes. The petrolatum was then slowly added and mixed in for about 5 minutes. Finally, the hydrated sodium silicate was added and mixed in for about 5 minutes. The batch size was about 466.44 grams.

The softness value of the putty, as determined using the method described above under the heading "Softness Value Measurement" was 6.32 mm. The expansion ratio of Example 21, based on an average of two determinations, was 2.76. The flow characteristic of the putty was excellent. Further, the "Flame Through Test" and the "Fire Hose Stream Test."

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

unvulcanized styrene butadiene rubbers, unvulcanized ethylene acrylic rubbers, unvulcanized nitrile rubbers, unvulcanized urethane rubbers, unvulcanized ethylene vinyl acetate rubbers, and combinations thereof.

5. The putty according to claim 4 wherein said putty comprises about 10 to about 50 percent by weight of said unvulcanized rubber, based on the total weight of said putty.

6. The putty according to claim 5 wherein said putty comprises about 50 to about 200 percent by weight of said intumescent material, based on the total rubber and unvulcanized rubber content of said putty.

7. The putty according to claim 4 wherein said putty further comprises a plasticizer, a char forming resin, a filler, and at least one of an antioxidant or an antiozonant.

8. The putty according to claim 4 wherein said putty further comprises a flame retardant, a plasticizer, a char forming resin, a filler, and at least one of an antioxidant or an antiozonant.

9. The putty according to claim 8 wherein said flame retardant is boric oxide.

10. The putty according to claim 4 wherein said putty having a softness value of at least 4.5 mm.

11. The putty according to claim 4 wherein said putty having a softness value of at least 5 mm.

19. An indefinitely conformable intumescent putty comprising a blend of intumescent material, rubber, and at least 10 percent by weight unvulcanized rubber, based on the total weight of the putty, said putty having a softness value of at least 4 mm, said putty containing less than 0.25 percent by weight halogen, said putty containing less than 0.25 percent by weight water other than bound water, wherein bound water is water that does not come off until the putty is heated to at least 100°C, and said putty containing less than 0.25 percent by weight rubber curing agent, based on the total weight of the putty.

20. The putty according to claim 19 wherein said bound water is water that does not come off until the putty is heated to at least 150°C.

21. The putty according to claim 19 wherein said bound water is water that does not come off until the putty is heated to at least 250°C.

22. The putty according to claim 21 wherein said rubber is selected from the group consisting of natural rubber, butyl rubbers, polybutadiene rubbers, synthetic isoprene rubbers, styrene butadiene rubbers, ethylene acrylic rubbers, nitrile rubbers, urethane rubbers, ethylene vinyl acetate rubbers, and combinations thereof, and said unvulcanized rubber is selected from the group consisting of unvulcanized natural rubber, unvulcanized butyl rubbers, unvulcanized polybutadiene rubbers, unvulcanized synthetic isoprene rubbers, unvulcanized styrene butadiene rubbers, unvulcanized ethylene acrylic rubbers, unvulcanized nitrile rubbers,

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16633

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K21/14 C09K21/02 C09K21/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 025 058 (ATSUYOSHI SENOO) 18 June 1991 see abstract; claims 1,2,6,7	1-30
Y	US,A,4 324 835 (KEEN) 13 April 1982 see abstract; claims 1,2; example 1; table A	1-30
Y	GB,A,2 092 599 (FURUKAWA) 18 August 1982 see abstract; claims 1,2,5; examples 1-7; table 1	1-30
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 388, 28 August 1989 & JP,A,11 035895 (FURUKAWA), 29 May 1989, see abstract	1-30

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 May 1996	22.05.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Nicolas, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16633

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5025058	18-06-91	CA-A,C	2017364	23-11-91
		JP-A-	1135895	29-05-89
		JP-B-	8023017	06-03-96
US-A-4324835	13-04-82	DE-A-	3018890	11-12-80
		FR-A,B	2458388	02-01-81
		GB-A,B	2052306	28-01-81
GB-A-2092599	18-08-82	JP-B-	1003232	20-01-89
		JP-A-	57131262	14-08-82
		AU-B-	529611	16-06-83
		AU-B-	8020582	23-09-82
		DE-A-	3204387	12-08-82